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COUNTRY	USSR	DATE OF INFORMATION 1953
SUBJECT	Scientific - Chemistry, radioactive isotopes	
HOW PUBLISHED	Thrice-monthly periodical	DATE DIST. /2 FEB 1954
WHERE PUBLISHED	Moscow	NO. OF PAGES 4
DATE PUBLISHED	11 Feb 1953	
LANGUAGE	Russian	SUPPLEMENT TO REPORT NO.

THIS IS UNEVALUATED INFORMATION

CONCERNING THE ADDITIVE PROPERTY OF SORET'S COEFFICIENTS

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Soret's coefficient for solutions is understood to be the ratio of the coefficients of thermal and of ordinary diffusion for the solute. In the stationary state, when the flow of the solute caused by a temperature gradient is balanced by the ordinary diffusion flow, the relative change in concentration for a temperature change of one degree is equal to Soret's coefficient, i.e.:

$$\frac{D'}{D} = - \frac{dn}{n} \frac{1}{dT} ,$$

where D' is the coefficient of thermal diffusion, and D is the coefficient of ordinary diffusion.

In the case of ideal solutions of strong electrolytes, as postulated by the thermodynamic theory of Soret's effect [1], the quantity D'/D can be represented as the arithmetical mean of the quantities characterizing the individual ions:

$$\frac{D'}{D} = \frac{z_2 \frac{Q_1^*}{kT^2} + z_1 \frac{Q_2^*}{kT^2}}{z_1 + z_2} ,$$

where z_1 and z_2 are the valences of the cation and anion, and Q_1^* and Q_2^* are the so-called heats of transfer of the individual ions. This type of additivity of Soret's coefficients can be shown from very elementary considerations. For simplicity's sake, we will limit ourselves to solutions of uniunivalent electrolytes.

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In the absence of any noticeable concentration gradient $\left(\left| D \frac{dn}{dx} \right| \ll \left| D' n \frac{dT}{dx} \right| \right)$, we can write for a stream of ions of different signs:

$$\tau_+ = -d'_+ n \frac{dT}{dx} - nv_+ e \frac{dU}{dx} ,$$

$$\tau_- = -d'_- n \frac{dT}{dx} + nv_- e \frac{dU}{dx} ,$$

where e is the charge of a univalent ion, v_+ and v_- are the mobilities of the ions, U is the potential of the internal electrical field in the solution ensuring the electroneutrality of the ion stream, and d'_+ and d'_- are coefficients characterizing individual mobilities of ions in the thermal field.

Since numerically:

$$\tau_+ = \tau_- = \tau = -D' n \frac{dT}{dx} ,$$

$$D' = \frac{d'_- v_+ + d'_+ v_-}{v_+ + v_-} . \tag{1}$$

But it is well known that:

$$D = \frac{2kT v_+ v_-}{v_+ + v_-} \; [2]. \tag{2}$$

From equations (1) and (2) it immediately follows that:

$$\frac{D'}{D} = \frac{d'_- v_+ + d'_+ v_-}{2kT v_+ v_-} = \frac{d'_-}{2kT v_-} + \frac{d'_+}{2kT v_+} ,$$

i.e., Soret's coefficient actually possesses the property of additivity.

Attempts to prove the theory by experiment [3] up to this time have been hampered by the lack of reliable experimental data, since the only satisfactory determinations of Soret's coefficient were carried out on solutions of comparatively high concentrations (> 0.1 N).

We undertook the determination of Soret's coefficients for solutions of lithium, sodium, cobalt, and lead salts with the aid of a separation column [3] consisting of two coaxial copper tubes, the external one heated by current, and the internal one cooled with water. The solution was placed in the space (a = 0.045 cm) between the tubes and was concentrated during the course of the experiment in the lower (cobalt salts, NaCl, $NaNO_3$, Na_2SO_4, Li_2SO_4, $Pb(NO_3)_2$) or upper (NaI, LiI) region cf the column. Above and below the column, the internal (cold) tube had recesses forming reservoirs having a volume of v = 6.7 cm^3. The length of the working part of the column was equal to 20.5 cm; the radius of curvature of the space between the tubes R was 1.7 cm. The temperature difference between the hot and cold walls Δ T(Δ T = 56° - 21° = 25°) was determined by thermocouples (a total of ten). This temperature difference remained constant within $\pm 1^o$ C. The solution in the reservoirs was agitated by means of stirrers. After a definite time had passed, the current was cut off and 5 cm^3 samples of the solution were removed from the upper and lower reservoirs.

The theory of the separation column with the reservoirs at the ends is given in a work by one of the authors [4]. At the start of the experiment, the concentration in the reservoirs changes linearly with time:

$$\frac{n_L}{n_o} \cdot 1 = 1 - \frac{n_u}{n_o} = \frac{B a^3 \rho \beta \; g (\Delta T)^2}{6! v \, \eta} \frac{D'}{D} \, t. \tag{3}$$

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Here n_o, n_u, and n_L are the concentrations of the solution, respectively, initially and in the upper and lower reservoirs; β is the coefficient of cubic expansion of the solution; ρ is the density; η is the viscosity; and $B = 2\pi R$.

Thus, in order to determine Soret's coefficient, it is sufficient to determine the quantity $\left(\dfrac{n_L}{n_o} - 1\right) = \left(1 - \dfrac{n_u}{n_o}\right)$ at one moment of time t during the period when this quantity varies linearly with time.

The results of our experiments in the case of cobalt salts are given in the appended figure. Deviations of individual determinations from the average are given in terms of the rms error.

The concentration of the solutions in the reservoirs was determined with the aid of radioactive indicators ($Co^{60}SO_4$, $CoS^{35}O_4$, $Co^{60}(NO_3)_2$, $Co^{60}Cl_2$, $Na_2S^{35}O_4$, NaI^{131}, $Li_2S^{35}O_4$, LiI^{131}, $Pb^{212}(NO_3)_2$), as well as with the aid of semimicrochemical methods using zincuranylacetate (NaCl, NaI, NaNO$_3$, Na_2SO_4) [5], [6]. The results of the experiments, whether carried out with different methods or with the aid of different indicators, agreed in a fully satisfactory manner. In the case of NaI, I^{131} radiation did not affect the concentration process.

After the value D'/D has been determined for a group of salt solutions having a common cation or anion, (e.g., the group $CoSO_4$, $CoCl_2$, $Co(NO_3)_2$), the additive property of Soret's coefficients permits us to make only one determination for an analogous salt of some group, such as Na_2SO_4, in order to calculate Soret's coefficients for all the other members of the group, i.e., NaCl and $NaNO_3$.

Using the results of our experiments, we calculated the Soret coefficients for dilute solutions of cobalt, lithium, sodium and lead salts (see appended table) with the aid of equation (3). The Soret coefficients determined from the experiment for other salts are given in the next to the last column of the table. Complete agreement between experimental and calculated values, within the limits of error of our measurements, was obtained.

If the heat of transfer of the chloride ion is arbitrarily taken to be zero, the heats of transfer of the individual ions can be calculated from the data of the appended table on Soret's coefficients. These heats are listed as follows:

Ion		Cl^-	I^-	NO_3^-	SO_4^{--}	Li	Na	Co	Pb
Heat of transfer	in kcal/mol	0	-0.7	0.25	0.7	0.0	0.4	1.9	2.1
	in e v/ion	0	-0.03	0.01	0.03	0.00	0.02	0.09	0.09

Had we known the values for the heats of transfer of the individual ions, we could have calculated the thermal diffusion potentials in solutions of strong electrolytes [3]. Experimental determination of the latter at the present time is practically impossible.

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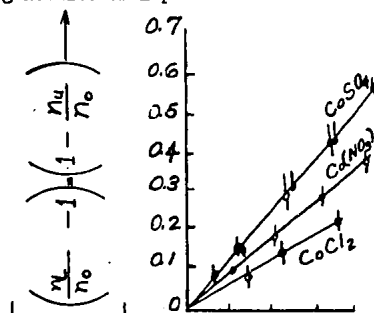
Figure showing Results of Experiments With Cobalt Salts

Table Showing Soret's Coefficients

Soln No	Solute	Concn of Initial Soln X 10^3 N	D'/D Measured X 10^3 (degree^{-1})	D'/D Calcd X 10^3 (degree^{-1})	No of Solns Used in Calcn
1	$CoSO_4$	1.0	6.7 ± 0.2	7.0 ± 0.5	2, 4, 5
2	$Co(NO_3)_2$	1.0	4.3 ± 0.2	3.9 ± 0.4	1, 4, 5
3	$CoCl_2$	1.0	3.3 ± 0.3	3.5 ± 0.4 / 3.2 ± 0.4	2, 5, 6 / 1, 4, 6
4	Na_2SO_4	1.0* / 2.0**	2.8 ± 0.3	2.3 ± 0.3	1, 2, 5
5	$NaNO_3$	4.0	1.7 ± 0.2	2.0 ± 0.4	1, 2, 4
6	NaCl	4.0	1.2 ± 0.2	1.0 ± 0.3 / 1.3 ± 0.3	2, 3, 5 / 1, 3, 4
7	NaI	4.0	-0.8 ± 0.1	-1.2 ± 0.5	4, 8, 9
8	Li_2SO_4	1.0	1.4 ± 0.1	0.9 ± 0.5	4, 7, 9
9	LiI	1.0	-2.3 ± 0.2	-1.8 ± 0.5	4, 7, 8
10	$Pb(NO_3)_2$	1.0	4.6 ± 0.2	-	-

*Concentration of solution tagged with $Na_2S^{35}O_4$.
**Concentration in the case of gravimetric determinations.

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